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1,2,7a-Trihydroxy-2-methylperhydro-1-phosphaindene 1-Oxide

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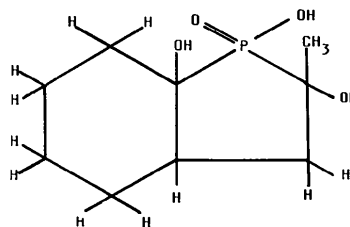
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Abstract. $C_9H_{17}O_4P$, $M_r = 220.20$, monoclinic, $P2_1$, $a = 12.385$ (4), $b = 6.590$ (3), $c = 13.394$ (4) Å, $\beta = 98.00$ (3)°, $V = 1082.54$ Å³, $Z = 4$, $D_x = 1.351$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 21.9$ cm⁻¹, $F(000) = 472$, $T = 296$ K, $R_F = 0.044$, $wR_F = 0.048$ for 1850 observed reflections [$I_o > 3\sigma(I_o)$] and 253 parameters. The asymmetric unit consists of two independent molecules which have almost identical but inverted conformations. Molecule 1: The five-membered phospholane ring exists in an envelope conformation with C(3) at the flap [the asymmetry parameter $\Delta C_s^{C(9)} = 2.35$ (6)°]. The six-membered cyclohexane ring is a slightly twisted chair [$\Delta C_s^{C(5)} = 1.93$ (6), $\Delta C_2^{C(3),C(4)} = 6.33$ (6)°]. The rings are *trans*-fused and the hydroxyl group O(4) is *anti* to the phosphoryl group P(1)—O(1). Molecule 2: The five-membered phospholane ring is a slightly twisted envelope with C(13) at the flap [$\Delta C_s^{C(13)} = 3.85$ (6)°]. The fused six-membered cyclohexane ring is almost an ideal chair [$\Delta C_s^{C(14),C(17)} = 1.08$ (6), $\Delta C_2^{C(13),C(18)} = 0.16$ (6)°]. The rings are *trans*-fused and the hydroxyl group O(14) is *anti* to the phosphoryl group P(2)—O(11).

Experimental. Colourless crystals of (I) from methanol/ethanol (1/1), 0.25 × 0.25 × 0.50 mm; CAD-4 diffractometer with graphite mono-

chromator; lattice parameters from the least-squares refinement of the setting angles of 22 reflections in the θ range 10–39°. Intensity data were collected by the ω -2 θ scan method with an ω -scan width of (1.80 + 0.14tan θ)° and a variable scan speed of 1.5–5.5° min⁻¹ using graphite-monochromatized Cu $K\alpha$ radiation with indices $h - 1$ to 15, $k - 1$ to 8 and $l - 16$ to 16 in the θ range 0–70°. The intensities of three standard reflections (312, 004, 215) measured every hour showed no evidence of crystal decay. Intensities of 2228 reflections were measured of which 1902 had $I > 3\sigma(I)$, and were used in the structure solution and refinement. Lorentz-polarization corrections and ψ -scan-based empirical absorption corrections were applied.



(I)

The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). Refinement of the structure was by full-matrix least-squares calculations. At an intermediate stage in the refinement, a difference map revealed all the H atoms which were included in the subsequent cycles of refinement at

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fixed distances, C—H = 1.00 Å. The H atoms of hydroxyl groups O(2), O(3), O(4), O(12), O(13) and O(14) were allowed to refine. The non-H atoms were refined anisotropically and an overall isotropic temperature factor was allowed for the H atoms bonded to C atoms. The structure obtained was consistent with the known chirality. Refinement converged with $R = 0.044$ and $wR = 0.048$. Maximum shift/e.s.d. was less than 0.1; final weighting scheme (Carruthers & Watkin, 1979), $w = A_0I_0(x) + A_1I_1(x) + A_2I_2(x)$ where I_i is the i th Chebyshev series, $x = F_o/F_o(\max)$; minimum and maximum electron density in the final difference map *ca* -0.3 and $0.3 \text{ e } \text{Å}^{-3}$; scattering factors from Cromer & Mann (1968). Anomalous-dispersion parameters from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations carried out on the University of Oxford Chemical Crystallography Laboratory VAX11/750 computer using *SHELXS86* (Sheldrick, 1985), *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985) and *CHEMGRAF* (Davies, 1981), and on an Amstrad PC1512SD microcomputer in Łódź using the *CSU* program (Vićković, 1988).

The final fractional coordinates are given in Table 1* and bond distances and angles for non-H atoms are in Table 2. The molecular structure with the crystallographic numbering scheme is depicted in Fig. 1.

Related literature. The structures of two related compounds: 7-benzyl-9-methoxy-8-phenyl-7-phosphacis-bicyclo[4.3.0]non-8-ene *anti*-7-oxide (Galdecki, 1979) and 7-benzyl-4-*tert*-butyl-9-hydroxy-8-phenyl-7-phosphacis-bicyclo[4.3.0]non-8-ene *anti*-7-oxide (Galdecki & Główka, 1980) have been reported.

The reaction sequence involving intramolecular 'double addition' of bis(trimethylsilyl) hypophosphite to simple 1,*n*-diketones in the presence of trimethylchlorosilane and triethylamine followed by ethanolation of the intermediate trimethyl phosphinites is an effective and stereoselective approach to the cyclic analogues of bis(1-hydroxyalkyl)-phosphinic acids containing a phospholane or phosphorinane ring (Bodalski, Krawczyk & Majewski, 1987a). Extension of this method to the asymmetric synthesis of the selected trihydroxyperhydrophosphindanes, bicyclic analogues of bis(1-hydroxyalkyl) phosphinic acids, gave the title compound. 2-(2'-Oxopropyl)cyclohexanone was used as a convenient starting diketone (Bodalski, Krawczyk & Majewski,

* Lists of anisotropic thermal parameters, H-atom positions, bond distances and angles involving H atoms, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53907 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* ($\text{Å}^2 \times 10^3$)

Molecule 1	x	y	z	U_{eq} *
P(1)	3823 (2)	-69	251 (2)	286
O(1)	4494 (4)	-735 (13)	-525 (5)	393
O(2)	4484 (5)	1196 (13)	1107 (6)	398
O(3)	3461 (6)	-4051 (12)	431 (7)	379
O(4)	2160 (4)	2335 (11)	500 (6)	317
C(1)	3180 (8)	-2174 (17)	881 (8)	324
C(2)	1975 (8)	-1824 (17)	620 (10)	319
C(3)	1794 (7)	-740 (16)	-378 (9)	286
C(4)	598 (7)	4 (25)	-797 (8)	434
C(5)	559 (7)	1181 (21)	-1767 (9)	456
C(6)	1327 (7)	2832 (20)	-1705 (10)	467
C(7)	2497 (7)	2228 (22)	-1278 (8)	426
C(8)	2534 (7)	1152 (16)	-264 (8)	276
C(9)	3540 (10)	-2262 (22)	2019 (9)	562
Molecule 2				
P(2)	1172 (2)	-139	4747 (2)	274
O(11)	483 (4)	505 (12)	5534 (6)	338
O(12)	553 (5)	-1452 (13)	3894 (6)	362
O(13)	1597 (5)	3832 (12)	4646 (7)	357
O(14)	2766 (5)	-2685 (13)	4556 (6)	358
C(11)	1780 (8)	2006 (16)	4106 (9)	287
C(12)	3038 (8)	1614 (20)	4449 (10)	358
C(13)	3218 (8)	454 (16)	5450 (9)	337
C(14)	4349 (7)	-167 (22)	5784 (8)	391
C(15)	4394 (9)	-1320 (23)	6789 (9)	531
C(16)	3581 (9)	-3255 (21)	6649 (10)	531
C(17)	2422 (7)	-2525 (19)	6275 (7)	372
C(18)	2421 (7)	-1395 (16)	5325 (9)	285
C(19)	1416 (9)	2166 (20)	3017 (8)	460

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* ($^\circ$)

Molecule 1		Molecule 2	
P(1)—O(1)	1.484 (7)	P(2)—O(11)	1.506 (7)
P(1)—O(2)	1.555 (8)	P(2)—O(12)	1.549 (8)
P(1)—C(1)	1.86 (1)	P(2)—C(11)	1.87 (1)
P(1)—C(8)	1.84 (1)	P(2)—C(18)	1.83 (1)
O(3)—C(1)	1.44 (1)	O(3)—C(11)	1.44 (1)
O(4)—C(8)	1.41 (1)	O(14)—C(18)	1.45 (1)
C(1)—C(2)	1.50 (1)	C(11)—C(12)	1.58 (1)
C(1)—C(9)	1.53 (1)	C(11)—C(19)	1.47 (1)
C(2)—C(3)	1.50 (2)	C(12)—C(13)	1.53 (2)
C(3)—C(4)	1.59 (1)	C(13)—C(14)	1.47 (1)
C(3)—C(8)	1.54 (1)	C(13)—C(18)	1.56 (1)
C(4)—C(5)	1.51 (2)	C(14)—C(15)	1.54 (2)
C(5)—C(6)	1.44 (2)	C(15)—C(16)	1.62 (2)
C(6)—C(7)	1.53 (1)	C(16)—C(17)	1.53 (1)
C(7)—C(8)	1.53 (1)	C(17)—C(18)	1.47 (1)
O(2)—P(1)—O(1)	112.8 (4)	O(12)—P(2)—O(11)	113.8 (4)
C(1)—P(1)—O(1)	114.5 (5)	C(11)—P(2)—O(11)	114.3 (5)
C(1)—P(1)—O(2)	106.3 (5)	C(11)—P(2)—O(12)	105.9 (5)
C(8)—P(1)—O(1)	114.1 (5)	C(18)—P(2)—O(11)	111.1 (5)
C(8)—P(1)—O(2)	112.5 (5)	C(18)—P(2)—O(12)	111.3 (5)
C(8)—P(1)—C(1)	95.3 (4)	C(18)—P(2)—C(11)	99.6 (5)
O(3)—C(1)—P(1)	107.9 (7)	O(13)—C(11)—P(2)	107.6 (7)
C(2)—C(1)—P(1)	104.7 (7)	C(12)—C(11)—P(2)	100.7 (7)
C(2)—C(1)—O(3)	108.9 (9)	C(12)—C(11)—O(13)	102.0 (9)
C(9)—C(1)—P(1)	113.4 (9)	C(19)—C(11)—P(2)	115.0 (8)
C(9)—C(1)—O(3)	109.3 (9)	C(19)—C(11)—O(13)	113.0 (10)
C(9)—C(1)—C(2)	112.4 (10)	C(19)—C(11)—C(12)	116.9 (9)
C(3)—C(2)—C(1)	107.5 (9)	C(13)—C(12)—C(11)	110.6 (9)
C(4)—C(3)—C(2)	118.5 (9)	C(14)—C(13)—C(12)	114.9 (10)
C(8)—C(3)—C(2)	106.4 (8)	C(18)—C(13)—C(12)	106.4 (8)
C(8)—C(3)—C(4)	107.3 (9)	C(18)—C(13)—C(14)	112.2 (9)
C(5)—C(4)—C(3)	112.3 (9)	C(15)—C(14)—C(13)	108.7 (9)
C(6)—C(5)—C(4)	113.4 (10)	C(16)—C(15)—C(14)	110.0 (9)
C(7)—C(6)—C(5)	114.0 (10)	C(16)—C(15)—C(18)	109.3 (10)
C(8)—C(7)—C(6)	111.2 (9)	C(18)—C(17)—C(16)	109.2 (8)
O(4)—C(8)—P(1)	109.0 (7)	O(14)—C(18)—P(2)	106.3 (7)
C(3)—C(8)—P(1)	99.0 (6)	C(13)—C(18)—P(2)	100.2 (7)
C(3)—C(8)—O(4)	105.5 (8)	C(13)—C(18)—O(14)	106.9 (8)
C(7)—C(8)—P(1)	117.0 (7)	C(17)—C(18)—P(2)	119.5 (7)
C(7)—C(8)—O(4)	114.5 (9)	C(17)—C(18)—O(14)	110.7 (9)
C(7)—C(8)—C(3)	110.1 (9)	C(17)—C(18)—C(13)	112.2 (9)

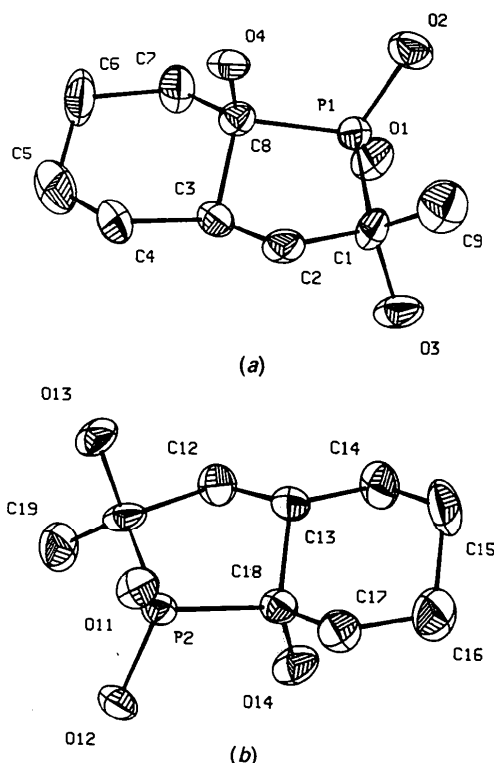


Fig. 1. CHEMGRAF (Davies, 1981) drawing of the asymmetric unit content showing the numbering scheme. (a) Molecule 1. (b) Molecule 2.

1987b). The synthesis and chemistry of the title compound will be reported elsewhere (Bodalski *et al.*, 1987b).

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3a,4,5-Trihydroxy-5,7,7-trimethylperhydro-4-phosphaindene 4-Oxide

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Abstract. C₁₁H₂₁O₄P·2H₂O, *M_r* = 284.28, monoclinic, *P*2₁/*n*, *a* = 6.818 (4), *b* = 12.956 (3), *c* = 32.854 (7) Å, β = 91.01 (3)°, *V* = 2901.81 Å³, *Z* = 8, *D_x* = 1.301 g cm⁻³, λ(Cu Kα) = 1.54178 Å, μ = 18.4 cm⁻¹, *F*(000) = 1232, *T* = 293 K, *R_F* = 0.045, *wR_F* = 0.049 for 3421 observed reflections [*F_o* ≥

3σ(*F_o*)] and 327 parameters. The asymmetric unit consists of two independent molecules existing in almost identical conformations. Molecule 1: The six-membered phosphorinane ring exists in a distorted chair conformation [the asymmetry parameters are Δ*C_s*^{P(1)} = 5.66 (6), Δ*C_s*^{C(1)} = 6.37 (6), Δ*C₂*^{C(1),C(2)} = 11.26 (6)°]. The five-membered cyclopentane ring is an envelope with C(4) at the flap [Δ*C_s*^{C(4)} = 10.07 (6)°]. Molecule 2: The six-membered phosphorinane ring is a distorted chair [Δ*C_s*^{P(2)} = 3.25 (6), Δ*C_s*^{C(21)} = 7.10 (6), Δ*C₂*^{C(22)} = 12.71 (6)°]. The five-

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